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TECHNICAL REPORT V

Contract N9onr-?5?01

Project Designation NR031-364

... MECHANICS OF SUBSTANCES
... VESSELS FOR LIQUID SODIUM,
POTASSIUM AND NaK.

Mine Safety Appliances Company

TECHNICAL REPORT V

Contract N9onr-85801

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THE THERMODYNAMICS OF SUBSTANCES USED AS
VESSELS FOR LIQUID SODIUM, POTASSIUM AND NaK.

by

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ABSTRACT

Interest in corrosion caused by sodium-potassium alloy has led to the calculation of the free energies of formation of the oxides of metals of possible interest as containers for the alloy or as "getters" for the alloy. The possibility of formation of sodium salts of the acidic metal oxides has also been considered. The data have been assembled into a free energy-temperature chart, from which favorable conditions, if any, for the reaction of a metal with the oxide of another metal may be read at a glance.

THE THERMODYNAMICS OF SUBSTANCES USED AS VESSELS FOR LIQUID SODIUM, POTASSIUM AND NaK.

The possible use of NaK alloy as a heat transfer medium makes important the collection of all possible data on its corrosive properties. Tests in these laboratories with small objects suspended in the hot metal have indicated that addition of oxygen to the liquid alkali metal greatly accelerates the corrosion of other metals. Hence a study of the thermodynamic properties of the oxides of elements of possible use in containers was deemed worthwhile.

A graphical presentation of the results is most advantageous from the standpoint of conciseness and clarity. The large chart at the end of this paper contains plots of the free energies of formation of the various oxides from the elements at the same temperature in the standard state versus the absolute temperature from 300° to 1000°K. This covers the entire liquid ange from the melting point to the boiling point of sodium, potassium and NaK. Where an element formed several oxides, the one having the highest free energy of formation per atom of oxygen was considered.

The possibility of the formation of sodium salts of the more acidic oxides was also considered. The chart contains plots of the free energy of formation of thee such salts. There is a marked paucity of data on such compounds and the plots may be far from accurate. Nevertheless they indicate the possibility of much greater corrosion of elements forming acidic oxides than of those forming solely basic oxides.

The possibility of using an element soluble in sodium to deoxidize the sodium and all other metals contacted (to act as a "getter") was also of interest. The oxides of several such metals are also plotted.

Glasses are affected by the molten metal. Hence the free energies of the reduction of silica and boron trioxide by sodium, the chief components of glasses with high softening temperatures, are also plotted on the chart.

Method of Calculation:

The free energies were calculated in every case from the definitive relationship:

$$(1) \quad \Delta F_f^{\,o} = \Delta H_f^{\,o} - T\Delta S_f^{\,o}$$

where ΔF is free energy change

ΔH is enthalpy (heat content) change

T is temperature in degrees Kelvin

ΔS is entropy change

f subscript signifies that the thermodynamic property refers to the effect accompanying the formation of the substance from the elements. The superscript ^{o} indicates that the reactants and products are in the standard state (that most common) under a pressure of 1 atmosphere.

Much of the data was taken from reference (1) which, for many of the compounds considered, listed the free energies of formation at 25°C and, for the elements and most of the compounds, the total entropies at 25°C. Most of the higher temperature data came from reference (2), which listed for the elements and compounds the increases in enthalpy $(H_T - H_{298.16})$

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and in entropy $(S_T - S_{298.16})$ above 25°C. For a few elements and oxides reference (1) part III gives more accurate absolute entropies at high temperatures which were used in preference to Kelley's data[2].

Again at the temperature T:

(2) $\Delta F^o_{f_T} = \Delta H^o_{f_T} - T\Delta S^o_{f_T}$

(3) $\Delta F^o_{f_{298.16}} - \Delta H^o_{f_{298.16}} - 298.16\Delta S^o_{f_{298.16}}$

subtracting (3) from (2)

(4) $\Delta F^o_{f_T} - \Delta F_{f_{298.16}} = (\Delta H^o_{f_T} - \Delta H^o_{f_{298.16}}) - T\Delta S^o_{f_T} - 298.16\Delta S^o_{f_{298.16}}$

Let $\Delta\Delta(f) =$ the increase in the value of the thermodynamic function over that at 25°C. Then

(5) $\Delta\Delta F^o_f = \Delta\Delta H^o_f - T(\Delta S^o_{f_{298.16}} + \Delta\Delta S^o_f) + 298.16\Delta S^o_{f_{298.16}}$

rearranging

(6) $\Delta\Delta F^o_f = \Delta\Delta H^o_f - (T - 298.16)\Delta S^o_{f_{298.16}} - T\Delta\Delta S^o_f$

The increases of enthalpy $(\Delta\Delta H^o_f)$ and entropy $(\Delta\Delta S^o_f)$ for the formation of the compound above those at 25°C were then calculated by subtracting these properties for the reactants from the same properties for the products. These values were substituted in equation (6) and the free energy of reaction at the temperature T was then computed by the relationship:

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$$(7) \quad \Delta F_{f_T} = \Delta F^o_{f_{298.16}} + \Delta \Delta F^o_f$$

A sample calculation of the free energies of formation of calcium oxide follows ($Ca + \frac{1}{2}O_2 \longrightarrow CaO$):

At 25°C (298.16°K)

$$\Delta F_f = -144,400 \text{ cal./mole}[1]$$

S^o's[1] in cal./mole-deg.

$CaO_{(s)}$ 9.5	$Ca_{(s)}$ 9.95	$1/2\ O_{2(g)}$ 24.50

$$\Delta S^o_f = 9.5 - (9.95 + 24.50) = -24.55$$

At 600°K

	$H_{600} - H_{298.16}$[2]	$S_{600} - S_{298.16}$[2]
$Ca_{(s)}$	2060	4.72
$1/2\ O_{2(g)}$	1105	2.55
Sum	3165	7.27
$CaO_{(s)}$	3400	7.82
$\Delta\Delta H_f$	235	$\Delta\Delta S_f$ 0.55

Again:

$$(6) \quad \Delta\Delta F_f = \Delta\Delta H_f - T\Delta\Delta S_f - (T - 298.16)\Delta S^o_f$$

$$= 235 - 600(0.55) - (302)(-24.55)$$

$$= +7309$$

$$\Delta F_{f_{600}} = \Delta F_{f_{298.16}} + \Delta\Delta F_f = -144,400 + 7309$$

$$= -137,091 \text{ cal.}$$

Similar calculations were made at 400°, 800° and 1000°K. It was soon noted that ΔF_f^o varied almost linearly with temperature; so that later calculations were made only for points at 25°C and 600° and 1000°K.

The sources of data for the various oxides (listed alphabetically), together with the reported accuracy of the data follow:

Oxide	Sources of Data	Accuracy
Aluminum (Al_2O_3)	1, 2	± 200 calories
Beryllium (BeO)	1, 2	± 1000 calories
Boron (B_2O_3)	1, 2	± 300 calories
Calcium (CaO)	1, 2	± 500 calories
Cesium (Cs_2O)	1	± 2000 calories

The entropy of Cs_2O at 25°C was estimated to be 30.5 by the method of Wenner[3] from the entropies of Cu_2O, Ag_2O, and Na_2O. Wenner has shown that the entropies of solids of similar types plotted versus the logarithms of their molecular weights give well defined straight lines. The plots used in this paper are given in the second small chart. No high temperature data was available.

Chromic oxide (Cr_2O_3)	1, 2	± 500 calories
Cuprous oxide (Cu_2O)	1, 2	± 500 calories
Ferrous chromite ($FeCr_2O_4$)	1, 2	± 500 calories
Iron oxide (magnetic)(Fe_3O_4)	1, 2	± 500 calories

This oxide had a greater free energy of formation per atom of oxygen than either ferrous or ferric.

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Lithium oxide (Li_2O)   1 $\div$ 2000 calories

The entropy of Li_2O at $25^{\circ}C$ was estimated to be

10.5 in the same manner as that of Cs_2O .

Magnesium oxide (MgO)   1, 2 $\pm$ 500 calories

Manganous oxide (MnO)   1, 2 $\pm$ 500 calories

Molybdenum dioxide (MoO_2)   1 $\pm$ 1000 calories

No high temperature data was available. S° at

$25^{\circ}C$ was estimated to be 18 by the method of Wenner[3]

from the chart on p. 176 for dioxides.

Nickel oxide   1, 2 $\pm$ 1000 calories

The increases in entropy of nickel oxide at high

temperatures over the entropy at $25^{\circ}C$ were calculated

by integrating the equation $dS = C_p \dfrac{dT}{T}$ over the

temperature range $298.16^{\circ}K$ to T. The heat capacity

equation used was that given by Seltz[4] to fit the

data of Kapustinskii[5]. The increases in enthalpy

for NiO were also calculated by integrating the equa-

tion $dH = C_p dT$ over the temperature range $298.16^{\circ}K$ to T.

Niobium tetroxide (Nb_2O_4)   1 $\pm$ 1500 calories

S° at $25^{\circ}C$ was estimated to be 28.5 by the

method of Wenner[3] from the values for V_2O_4 and

Sb_2O_4 No high temperature data was available

Niobium pentoxide (Nb_2O_5)   1, 2 $\pm$ 1500 calories

S° at $25^{\circ}C$ was estimated to be 32.5 by the method

of Wenner[3] from the values for V_2O_5, and Ta_2O_5

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Potassium monoxide (K_2O) 1 $\pm$ 10,000 calories

S^o at 25^oC was estimated to be 21 by the method and data used for Cs_2O. Kireev[6] gives 26.5 for S^o from additivity calculations based on the alums. This value was used. The high temperature entropies and enthalpies of K_2O were taken by subtracting the values for kyanite (Al_2SiO_5) and three moles of quartz (SiO_2) from those of two moles of microcline ($KAlSi_3O_8$). The entropies and enthalpies of many complex substances are fairly closely equal to the sum of these properties for their constituents[9,10,12].

Rubidium monoxide (Rb_2O) 1 $\pm$ 10,000 calories

S^o at 25^oC was estimated to be 26.5 by the same method and data used for Cs_2O.

Silicon dioxide (SiO_2 vitreous) 1, 2 $\pm$ 500 calories

Sodium monoxide (Na_2O) 1, 2 $\pm$ 2000 calories

The ΔH_f^o for Na_2O at 25^oC was calculated from Ketchen's value[7] ($-44,360 \pm 60$ cal./g. atom) for the heat of solution of sodium in water, Roth's value[8] for the heat of solution of Na_2O in water, and the heat of formation of water. The entropies for Na_2O at all temperatures are taken from those of the sodium silicates and titanates and are subject to the inaccuracies of the additivity principle;[9] e.g., $S_{298.16}^o$ is given as 17.4 in reference (1). This value is a mean of values from 16.2 to 18.7 and is based in part on an inaccurate value for $S_{298.16}^o$ for rutile, but is

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the best available. The entropies and heat contents of sodium at high temperatures were taken from reference (13). The slope of the Na_2O free energy-temperature plot is suspiciously steep compared with those of the other oxides.

Titanium monoxide (TiO)   1, 2 $\pm$ 1000 calories

ΔF_f at 25°C was estimated to be 142 kcal./mole from the ΔF_f's of Ti_3O_5, Ti_2O_3, and TiO_2. The increments in ΔF_f between the successively heavier oxides were almost exactly equal to ΔF_f for TiO_2.

Vanadium dioxide (V_2O_2)   1 $\pm$ 200 calories

S° at 25°C was estimated by the method and data of Wenner[3] (p. 177) to be 11 for the formula VO or 22 for the formula V_2O_2. Since no high temperature heat capacity data was available for this oxide, and the data for the trioxide (V_2O_3) was available with high accuracy, reference (2) part III, the free energy-temperature relationship for the latter oxide was plotted.

Zirconium dioxide   2, 3 $\pm$ 300 calories
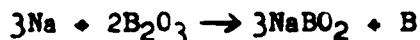
<u>Sodium salts of acidic oxides:</u>

Sodium meta aluminate ($NaAlO_2$) 1, 2 $\pm$ 2000 calories

S° at 25°C was estimated to be 25, using the method of Wenner[3] and the data for $AgNO_2$ and $AgClO_2^1$. Although these are quite dissimilar compounds, they were the best available for estimation. The high temperature entropies were taken by subtracting three times

the values for the difference in entropies of $Na_2Si_2O_5$ and Na_2SiO_3 from the entropies of albite $(NaAlSi_3O_8)$[3]. Since the reaction of interest $(2Na_2O + Al \longrightarrow NaAlO_2 + 3Na$ or $4 Na_2O + 2Al \longrightarrow Na_2O \cdot Al_2O_3 + 6Na)$ involves the reduction of 3 moles of Na_2O by the formation of 2 moles of $NaAlO_2$. The plot is of 2/3 the ΔF_f of $NaAlO_2$.

Sodium metaborate $(NaBO_2)$ 1, 2 $\pm$ 1500 calories

S^O at 25°C was estimated to be 23 by the method used for $NaAlO_2$. This product is chiefly of interest in glass; so the reaction plotted is:

$$3Na + 2B_2O_3 \longrightarrow 3NaBO_2 + B$$

Only the point at 25°C was plotted since no high temperature data on $NaBO_2$ was available.

Sodium chromite $(NaCrO_2)$ $\pm$ 5000 calories

The difference in the ΔH_f's of $Na_2Cr_2O_4$ and $FeCr_2O_4$ was assumed to be the same as that between Na_2SiO_3 and $FeSiO_3$ $\left[-363 - (-276) = -87 \text{ kcal./mole} \right]$. $\Delta H_{f_{298.16}}$ was given the value $-342 + (-87) = -429$ kcal./mole. By the method of Wenner[3], $S^O_{298.16}$ was estimated to be 47 (for $Na_2Cr_2O_4$) based on the data for $MgCr_2O_4$ and $FeCr_2O_4$, with an addition of 12 for a salt with 2 cations instead of 1. Using the method given for $NaAlO_2$ a value of 27 was estimated for $NaCrO_2$ or 54 for $Na_2Cr_2O_4$. As a mean, a value of 25 for $NaCrO_2$ or 50 for $Na_2Cr_2O_4$ was used. No high temperature data was available, so the slope was plotted parallel to that of $NaAlO_2$. The plot, like that of $NaAlO_2$, is 2/3 ΔF_f versus T.

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Sodium silicate (Na_2SiO_3)   1, 2 $\pm$ 500 calories

The reaction of interest is the effect of sodium

on glass. $4Na + 3SiO_2 \longrightarrow 2Na_2SiO_3 + Si$

DISCUSSION AND CONCLUSIONS

It is noteworthy that the oxides of all except the most
noble elements, e.g. gold and platinum are thermodynamically
stable at room temperature. Corrosion control of economically
practical structural metals then resolves itself into the prob-
lem of protecting the metal from attack by oxygen by the form-
ation of a protective coating or by "gettering or anodizing".
The latter can be done by the direct application of a positive
electrical potential or by connection with a more electro-
positive element "a getter". Magnesium is most commonly used
for this purpose. Many metals form self-protecting adherent
oxide coatings. Chromium forms such a coating. Iron does
not; but the addition of ten per cent or more chromium causes
the entire oxide coating of the resulting alloy to be adherent.
The free energy of formation of chromic oxide indicates that
chromium should not be oxidized by sodium oxide at temperatures
below 880°Kelvin or 1100°Fahrenheit. But the stainless steels
largely used as NaK containers depend on an adherent oxide
coating for corrosion protection. The known amphoterism of
chromic oxide makes probable its reaction with sodium oxide
to form sodium chromite, and it may well be possible that the
ferric oxide also reacts to form sodium ferrite. Nickel (II)
oxides does not have reported acidic properties. Reaction of
sodium oxide with the stainless steel oxide until all the

chronic and ferric oxide had reacted would explain the observation in this laboratory that the stainless steel absorbs oxygen from sodium oxide for a time and then ceases to absorb it. Since the postulated sodium chromite and sodium ferrite do not appear in the titration analysis, they must be either adherent or insoluble in liquid sodium or potassium.

The fact that sodium chromite formation from sodium oxide and chromium appears to be energetically favored at all temperatures, complicates the picture. ($2Na_2O + Cr \longrightarrow NaCrO_2 + 3Na$). Factors favoring the reverse reaction, however, are the continual presence of a large excess of liquid sodium, the small quantity of chromium available at the steel surface, and the solid state of all the reactants except sodium at operating temperatures.

Two avenues for corrosion prevention seem to be open. The first is use of a metal as a container which forms an adherent basic oxide coating. Nickel fits these requirements admirably. Copper has the desired thermodynamic properties, but is somewhat soluble in hot sodium and the oxide is not adherent. The second means of prevention appears to be "gettering" with calcium or magnesium dissolved in the liquid sodium or potassium. From the thermodynamic properties either of these metals should "getter" any oxide or chromite formation in a sodium-stainless steel system.

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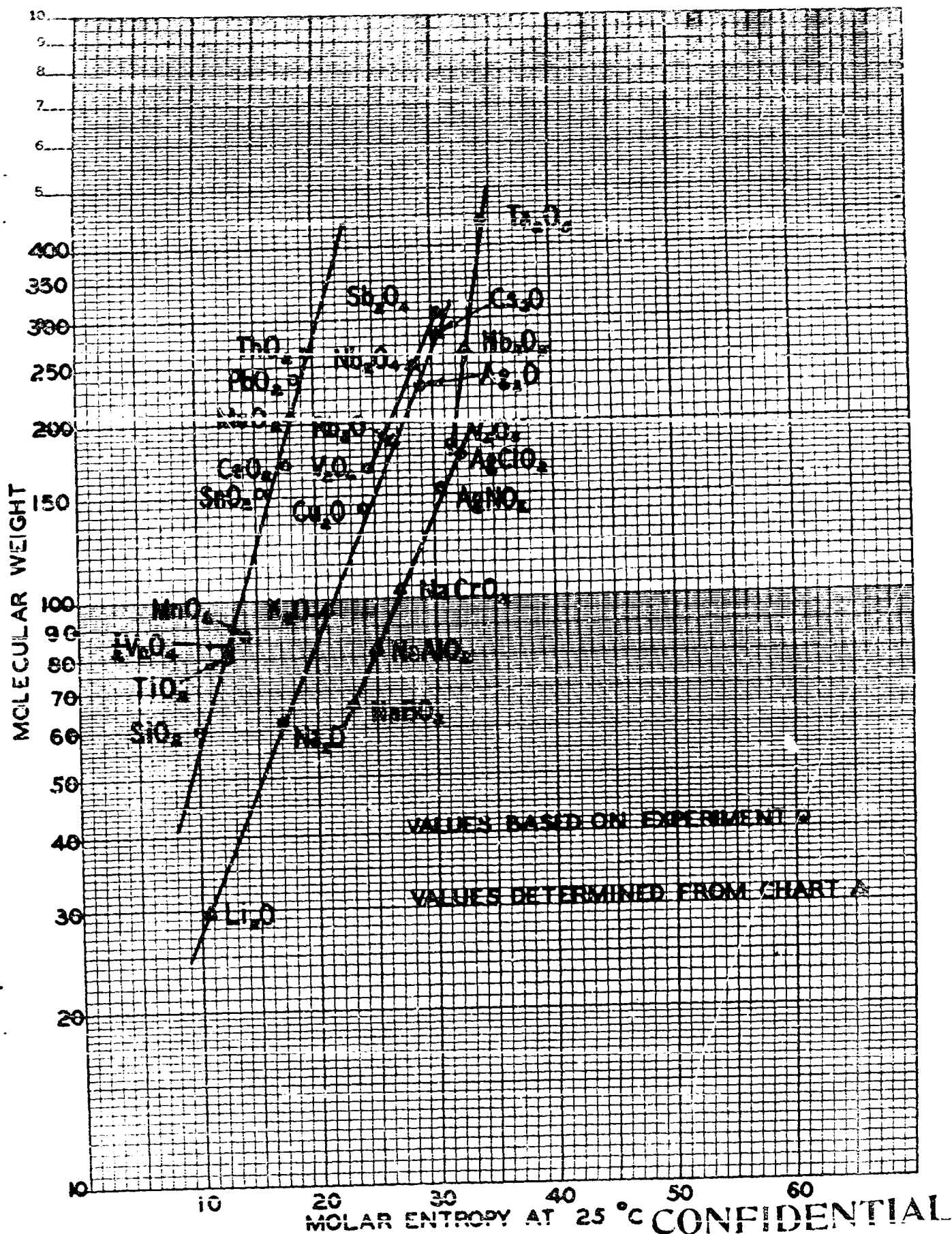cept sodium at operating temperatures.

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VALUES BASED ON EXPERIMENT 2

VALUES DETERMINED FROM CHART A

MOLECULAR WEIGHT

MOLAR ENTROPY AT 25 °C CONFIDENTIAL

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